

## VI.2 Photo-Activated Low Temperature, Fuel Cell Power Source

### Objectives

- Investigate photoactivation as a means of deconvoluting the role of charge transfer from other rate limiting steps controlling electrode kinetics in SOFC structures.
- Evaluate the potential for reduced temperature operation with improved conversion efficiencies, extended life, simplified fabrication and reduced cost.

### Accomplishments

- Demonstrated reduction in electrode impedance of a  $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$  ( $x = 0.35$ ) model electrode by 73% under low intensity illumination.
- Completed design and construction of high temperature Kelvin probe for in situ work-function and surface photovoltage spectroscopy.

### Introduction

Fuel cells convert the chemical energy stored in hydrogen or hydrocarbon fuels to electrical energy via electrochemical reactions at the anode and cathode. They offer higher efficiency and reduced emissions of greenhouse gases, such as  $\text{CO}_2$ , compared to conventional combustion processes. SOFCs, in particular, offer unrivaled energy conversion efficiency and fuel flexibility and therefore are expected to play a key role in the forthcoming hydrogen economy era. At present, however, SOFCs are too expensive for commercial applications. The high cost of this technology is largely due to the use of expensive refractory materials that need to operate at temperatures as high as  $1,000^\circ\text{C}$  in conventional SOFC designs. These high temperatures are required to reduce the ohmic

resistance of the oxygen-ion electrolyte (typically yttria-stabilized zirconia, YSZ) in large-scale SOFCs. The use of thinner electrolytes ( $\sim 10\text{ }\mu\text{m}$ ) in intermediate temperature (IT)-SOFCs and thin film electrolytes ( $\ll 1\text{ }\mu\text{m}$ ) in micro-SOFCs, currently being examined as alternative power sources for portable electronic devices, however, ensure short diffusion paths and correspondingly low ohmic resistances, thereby putting the burden of performance largely on the electrodes. Finding methods to increase the electrochemical performance of the electrodes is thus a key enabling technology for high performance micro-SOFCs designed to operate at moderate temperatures. Achieving improvements in electrode kinetics is important, as well, for increasing the power output of IT-SOFCs of traditional size scales. Unfortunately, despite many years of research, much remains unclear regarding the dominant loss mechanisms and limiting reaction steps at the electrodes. Therefore, it has been difficult to develop new electrodes that meet the demands for high electrochemical performance at reduced operation temperatures.

### Approach

This research aims at exploring the use of light as a means of deconvoluting the role of charge transfer from other steps involved in the electrode kinetics. In addition, thin film electrodes with well defined patterns, obtained by lithography and etching techniques, are used to overcome limitations related to the complex microstructures achieved at the electrode/electrolyte interface following powder processing and sintering routes typically used in conventional SOFC designs. Success along these lines is expected to lead to improved understanding of the electrode reaction mechanism and the rate limiting step(s) in SOFC and provide guidelines to design new electrodes with enhanced electrochemical performance.

In this study, illumination is utilized in several important ways. First, illumination is a means for generating excess electron-hole pairs and thereby investigating the role that minority electronic charge carriers play in the charge transfer reaction. The changes induced by illumination in the magnitude of the electrode impedance, and the activation energy which characterizes it, will provide direct evidence for the role of specific electronic charge carriers in controlling electrode kinetics. Second, the wavelength dependence of illumination serves as a powerful tool in investigating the role of localized versus delocalized states in the electronic band structure of the model electrode system,  $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$  (STF), in which the band structure as well as the level of mixed ionic-electronic

Harry Tuller (Primary Contact),  
Avner Rothschild

Massachusetts Institute of Technology  
Department of Materials Science & Engineering  
77 Massachusetts Ave., Room 13-3126  
Cambridge, MA 02139  
Phone: (617) 253-6890; Fax: (617) 258-5749  
E-mail: tuller@mit.edu

DOE Project Manager: Lane Wilson  
Phone: (304) 285-1336  
E-mail: Lane.Wilson@netl.doe.gov

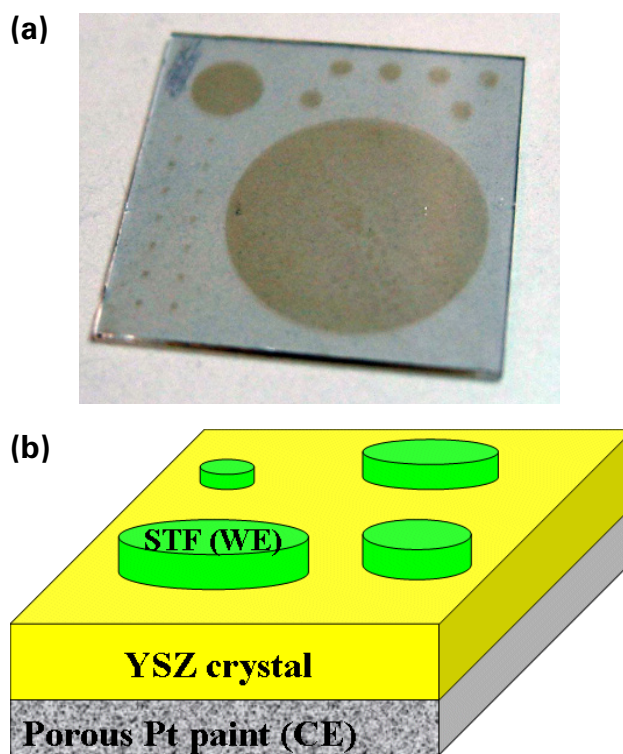
conduction can be manipulated by controlling the fraction of Fe substitution for Ti [1]. Further insight is obtained by carrying out spectroscopic measurements using monochromatic light to probe surface states (e.g., ionized oxygen anions) and correlating the surface exchange kinetics with their energy levels with respect to the band structure of the cathode material. This is achieved with the use of surface photovoltage spectroscopy (SPS) measurements [2].

## Results

$\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$  targets with  $x = 0.05$  (STF05) and 0.35 (STF35) were prepared by a conventional solid-state reaction method using commercial  $\text{SrCO}_3$ ,  $\text{TiO}_2$ , and  $\text{Fe}_2\text{O}_3$  powders. The powders were mixed in appropriate amounts to obtain the desired compositions, ball milled for 2 h, and subsequently calcined in air at  $1,200^\circ\text{C}$  for 15 h. Phase and chemical compositions were examined by x-ray diffraction (XRD) and x-ray energy dispersion spectroscopy (EDS). Subsequently, the STF powders were pressed into 1-inch pellets and sintered in a tube furnace at  $1,400^\circ\text{C}$  in air for 10 h. The pellets' density was about 93% of the theoretical density.

Thin film (film thickness between 65 and 230 nm) electrodes of STF35 were deposited by pulsed laser deposition (PLD) on YSZ solid electrolyte (SE) substrates (double-side polished, 100 direction, oriented crystals,  $15 \times 15 \times 0.5 \text{ mm}^3$ ) as shown in Figure 1a. STF35 electrodes of different area and triple phase boundary (TPB) length were prepared in order to examine the reaction path of the oxygen reduction reaction (ORR) in the dark and under illumination. The small area micro-electrodes ensure that their resistance dominates the overall resistance of the electrochemical test structures depicted in Figure 1b wherein the resistance of the counter electrode at the bottom of the SE substrate is negligible due to the respective size ratio. The STF35 films were shown via XRD to be polycrystalline and of the expected perovskite structure. Some degree of preferential orientation along the (100) direction was observed. The chemical composition of the films was examined using Rutherford Backscattering Spectrometry (RBS) and it was found to be commensurate with the composition of the target material (STF35).

The electrode resistance of the STF35 shown in Figure 1a was measured by electrochemical impedance spectroscopy (EIS) using electrochemical test structures as depicted in Figure 1b. These measurements were carried out in a unique microprobe system equipped with gas, temperature, and illumination controls that was recently constructed in our laboratory. The system comprises a stainless steel vacuum chamber with a temperature controlled stage capable of reaching up to  $1,200^\circ\text{C}$  in air or other gas atmospheres. The chamber is equipped with four micro-manipulators for



**FIGURE 1.** (a) STF35 Thin Film (65 nm) Electrodes on YSZ Substrate ( $15 \times 15 \text{ mm}^2$ ); (b) Schematic Diagram of the Electrochemical Test Structure

making contact to micro-patterned electrodes, with  $\sim 1 \mu\text{m}$  spatial resolution. State-of-the-art equipment is available to carry out a wide variety of electrical and electrochemical measurements in the DC and AC domains. An illumination system consisting of a 100 W quartz-tungsten-halogen (QTH) light source, monochromator, and fiber optics (Oriel) enables sample illumination for investigating the effect of photons on the electrode resistance and other electrochemical properties of the sample. The wavelength and intensity of the incident light can be varied in a controlled manner. A picture of the system is shown in Figure 2.

An exemplary impedance spectrum with the large STF35 (65 nm thick) electrode as the working electrode (WE) and porous Pt electrode as counter electrode (CE) is shown in Figure 3. This measurement was carried out in the dark, at  $400^\circ\text{C}$ , under flow of 400 sccm of dry air. No DC polarization was applied between the WE and the CE. The different contributions to the overall impedance response of the samples were analyzed using the equivalent circuit model shown in the inset of Figure 3. This model circuit includes contributions from the series resistance of the electrodes and electrical leads ( $R_1$ ), the SE impedance ( $R_2$  and  $\text{CPE}_2$ ), the constriction impedance of the SE ( $R_3$  and  $\text{CPE}_3$ ), and the CE and WE electrodes impedances ( $R_4$  and  $\text{CPE}_4$  and  $R_5$  and  $\text{CPE}_5$ ).



FIGURE 2. Photograph of the Microprobe Characterization System

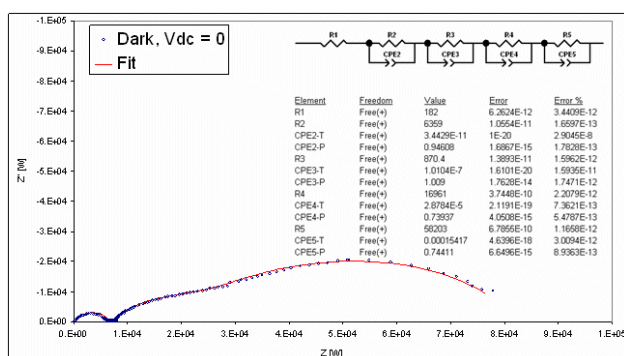


FIGURE 3. Impedance spectrum with the large STF35 electrode (cf. Figure 1a) serving as the WE, at  $T = 400^\circ\text{C}$ , in air (flow rate = 400 sccm), under dark condition, with no DC polarization applied between the WE and CE. The inset shows the equivalent circuit and the resultant values of the circuit elements.

Figure 4 compares the impedance response, under anodic bias of 100 mV applied to the STF electrode (the WE), in the dark and under full (broadband) illumination of the light source (no filters or grids were used in this measurement). Note that the illumination power is considerably reduced from the source (100 W) to sample. We expect the reduction in power intensity to be at least 90-95%. On top of that, the illuminated area is  $\sim 1,000 \text{ mm}^2$ , whereas the STF electrode area is only  $\sim 60 \text{ mm}^2$ . Thus, the effective illumination power is estimated to be approximately 300-600 mW, which includes the entire spectral bandwidth (between 200 and 2,000 nm). We expect that only a small fraction of this bandwidth in the UV range ( $\sim 200\text{-}400 \text{ nm}$ ) is effectively absorbed by the STF electrode, further reducing the effective illumination power to  $\sim 30\text{-}60 \text{ mW}$  or less. Yet, the electrode impedance was reduced by 73% under illumination, as shown in Figure 4.

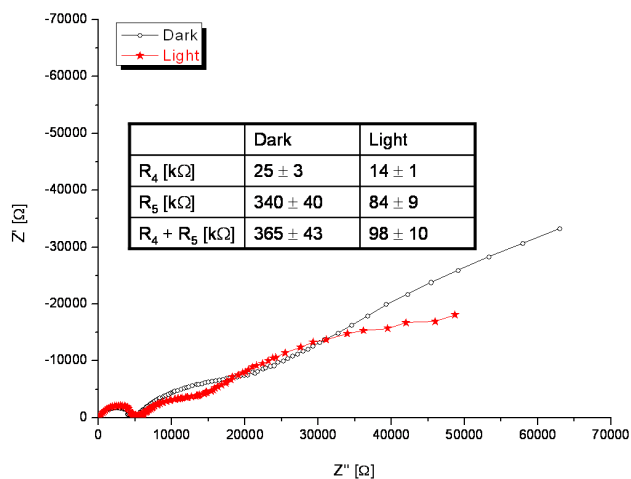


FIGURE 4. Impedance spectra with the large STF35 electrode (cf. Figure 1a) serving as the WE, at  $T = 400^\circ\text{C}$ , in air (flow rate = 400 sccm), under anodic polarization of 100 mV applied between the WE (+) and CE (-). The response under dark is shown in black, the response in low-power broadband light conditions shown in red. The inset table shows the respective electrode resistances  $R_4$  and  $R_5$ .

## Conclusions and Future Directions

- Illumination of a model electrode-electrolyte interface demonstrated the ability to modulate electrode impedance; future work to further characterize this phenomenon includes:
  - Examining compositions (x) of the model electrode  $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$  in which the band structure as well as the level of mixed ionic-electronic conduction can be manipulated by controlling fraction of Fe substitution for Ti.
  - Carrying out spectroscopic measurements using monochromatic light to probe surface states and correlating surface exchange kinetics with their energy levels achieved with use of surface photovoltage spectroscopy (SPS) measurements.
  - Modeling the role of photogenerated carriers in controlling charge transfer limited processes.

## References

1. A. Rothschild, W. Menesklou, H. L. Tuller, and E. Ivers-Tiffée, "Electronic Structure, Defect Chemistry, and Transport Properties of  $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-y}$  Solid Solution," *Chem. Mater.* (in print).
2. A. Rothschild, A. Levakov, Y. Shapira, N. Ashkenasy and Y. Komem, "Surface Photovoltage Spectroscopy Study of Reduced and Oxidized Nanocrystalline  $\text{TiO}_2$  Films," *Surf. Sci.* **532-535** (2003) 456-460.

### FY 2006 Publications/Presentations

1. A. Rothschild, W. Menesklou, H. L. Tuller, and E. Ivers-Tiffée, "Electronic Structure, Defect Chemistry, and Transport Properties of  $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-y}$  Solid Solution," Chem. Mater. (in print).
2. H.L. Tuller, "Some Insights Derived from the Study of Lithographically Defined Electrodes," U.S. Department of Energy- University of Florida High Temperature Electrochemistry Center Workshop: Fundamental Mechanisms of SOFC Cathode Reactions, Cocoa Beach, FL, January, 2006.
3. H.L. Tuller, "Micro-ionics: Prospects for Micro-Fuel Cells, Micro-Sensor Arrays and New Science," Pacific Northwest National Laboratory, Richland, WA, May, 2006.
4. H.L. Tuller, "Prospects for Micro-ionic Devices," National Microelectronics Centre Barcelona, Spain, June 23, 2006.